Received from D. Jones 4/3/91

Copy to John Gilks NEIC 4/4/91 MK

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PLEASE REPLY TO: SAN FRANCISCO

March 26, 1991

Mr. David M. Jones
Assistant Regional Counsel
Environmental Protection Agency
Region 9
75 Hawthorne Street
San Francisco, CA 94105

RE: Petroleum Recycling Corporation
Docket No. TSCA-09-91-0002

Dear Mr. Jones:

This is in response to your letter dated March 18, 1991.

PRC follows US EPA Method 9076 (Test Method for Total Chlorine In New and Used Petroleum Products by Oxidative Combustion and Microcoulometry) to determine the concentration of total halides. A copy of Method 9076 is enclosed (exhibit 1). Also enclosed is a laboratory report (Prequalification Survey) showing the results of the application of this test method on a sample of waste material (exhibit 2).

PRC follows Method 8080 (Organochlorine Pesticides and PCBs) to determine PCB concentration. A copy of this test method is enclosed (exhibit 3). Also enclosed are the gas chromatographic peaks from a sample of waste analyzed for PCB concentration on March 3, 1991 (exhibit 4).

If you have any questions regarding the enclosed materials, please do not hesitate to contact me.

Very truly yours,

JAFFE, TRUTANICH, SCATENA & BLUM

Marg Pietrasz

MARGARET A. PIETRASZ

156-374
enclosure

cc: John Markley
Kathleen Tripple

EXHIBIT

1

ROSEMOUNT ANALYTICAL INC.

DOHRMANN

Technical Reprint

TR-024

US EPA METHOD 9076

TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS BY OXIDATIVE COMBUSTION AND MICROCOULOMETRY

EPA METHOD 9076

TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS BY OXIDATIVE COMBUSTION AND MICROCOULOMETRY

1.0 SCOPE AND APPLICATION

1.1 This test method covers the determination of total chlorine in new and used oils, fuels and related materials, including crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by oxidative combustion and microcoulometry. The chlorine content of petroleum products is often required prior to their use as a fuel.

1.2 The applicable range of this method is from 10 to 10,000 ug/g chlorine.

2.0 SUMMARY OF METHOD

2.1 The sample is placed in a quartz boat at the inlet of a high temperature quartz combustion tube. An inert carrier gas such as argon, carbon dioxide, or nitrogen sweeps across the inlet while oxygen flows into the center of the combustion tube. The boat and sample are advanced into a vaporization zone of approximately 300°C to volatilize the light ends. Then the boat is advanced to the center of the combustion tube, which is at 1,000°C. The oxygen is diverted to pass directly over the sample to oxidize any remaining refractory material. All during this complete combustion cycle, the chlorine is converted to chloride and oxychlorides, which then flow into an attached titration cell where they quantitatively react with silver ions. The silver ions thus consumed are coulometrically replaced. The total current required to replace the silver ions is a measure of the chlorine present in the injected samples.

2.2 The reaction occurring in the titration cell as chloride enters is:

$$Cl^- + Ag^+ \longrightarrow AgCl\ (s)$$

The silver ion consumed in the above reaction is generated coulometrically thus:

$$Ag^\circ \longrightarrow Ag^+ + e^-$$

2.3 These microequivalents of silver are equal to the number of microequivalents of titratable sample ion entering the titration cell.

3.0 INTERFERENCES

3.1 Other titratable halides will also give a positive response. These titratable halides include HBr and HI (HOBr + HOI do not precipitate silver). Because these oxyhalides do not react in the titration cell, approximately 50% microequivalent response is detected from bromine and iodine.

3.2 Fluorine as fluoride does not precipitate silver, so it is not an interferent, nor is it detected.

3.3 This test method is applicable in the presence of total sulfur concentrations of up to 10,000 times the chlorine level.

4.0 APPARATUS AND MATERIALS

4.1 Combustion furnace. The sample should be oxidized in an electric furnace capable of maintaining a temperature of 1,000°C to oxidize the organic matrix.

4.2 Combustion tube. Fabricated from quartz and constructed so that a sample, which is vaporized completely in the inlet section, is swept into the oxidation zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube connects to a boat insertion device where the sample can be placed on a quartz boat by syringe, micropipet, or by being weighed externally. Two gas ports are provided, one for an inert gas to flow across the boat and one for oxygen to enter the combustion tube.

4.3 Microcoulometer, having variable gain and bias control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. The microcoulometer output signal shall be proportional to the generating current. The microcoulometer may have a digital meter and circuitry to convert this output signal directly to nanograms or micrograms of chlorine or micrograms per gram chlorine.

5.12 Cell Type 2.

5.12.1 Sodium acetate, CH_3CO_2Na.

5.12.2 Potassium Nitrate, KNO_3.

5.12.3 Potassium chloride, KCl.

5.12.4 Sulfuric acid (concentrated), H_2SO_4.

5.12.5 Agar, (jelly strength 450 to 600 g/cm^2).

5.12.6 Cell electrolyte solution - 85% acetic acid, combine 150 mL water (Step 5.2) with 1.35 g sodium acetate (Step 5.12.1) and mix well; add 850 mL acetic acid (Step 5.3) and mix well.

5.12.7 Dehydrating solution - Combine 95 mL sulfuric acid (Step 5.12.4) with 5 mL water (Step 5.2) and mix well.

CAUTION: This is an exothermic reaction and may proceed with bumping unless controlled by the addition of sulfuric acid. Slowly add sulfuric acid to water. Do not add water to sulfuric acid.

5.12.8 Potassium nitrate (10%), KNO_3. Add 10 g potassium nitrate (Step 5.12.2) to 100 mL reagent water (Step 5.2) and mix well.

5.12.9 Potassium nitrate (1M), KNO_3. Add 10.11 g potassium nitrate (Step 5.12.2) to 100 mL reagent water (Step 5.2) and mix well.

5.12.10 Potassium chloride (1M), KCl. Add 7.46 g potassium chloride (Step 5.12.3) to 100 mL water (Step 5.2) and mix well.

5.12.11 Agar bridge solution - Mix 0.7 g agar (Section 5.12.5), 2.5 g potassium nitrate (Section 5.12.2), and 25 mL reagent water (Section 5.2) and heat to boiling.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Collect a sample of oil representative of the source being sampled using the appropriate SW-846 sampling method. Because the collected sample will be analyzed for total halogens, it should be kept headspace free and refrigerated prior to preparation and analysis to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

6.2 Laboratory subsampling of the sample should be performed on a well-mixed sample of oil.

7.0 PROCEDURES

7.1 Preparation of apparatus

7.1.1 Set up the analyzer as per the equipment manufacturer's instructions.

7.1.2 Typical operating conditions: Type I.

Furnace temperature	1,000°C
Carrier gas flow	43 cm^3/min
Oxygen gas flow	160 cm^3/min
Coulometer	
Bias	250 mV
Gain	25%

7.1.3 Typical operating conditions: Type II.

Furnace temperature	H-1 850° C
	H-2 1,000°C
Carrier gas flow	250 cm^3/min
Oxygen gas flow	200 cm^3/min
Coulometer	
End point potential (bias)	
Gain G-1	1.5 coulombs/mV
G-2	3.0 coulombs/mV
G-3	3.0 coulombs/mV
ES-1 (range 1)	25 mV
ES-2 (range 2)	30 mV

NOTE: Other conditions may be appropriate. Refer to the instrumentation manual.

7.2 Sample introduction.

7.2.1 Carefully fill a 10-uL syringe with 2 to 5 uL of sample depending on the expected concentration of total chlorine. Inject the sample through the septum onto the cool boat, being certain to touch the boat with the needle tip to displace the last droplet.

7.2.2 For viscous samples that cannot be drawn into the syringe barrel, a positive displacement micropipet may be used. Here, the 2-5 uL of sample is placed on the boat from the micropipet through the opened hatch port. The same technique as with the syringe is used to displace the last droplet into the boat. A tuft of quartz wool in the boat can aid in completely transferring the sample from the micropipet into the boat.

8.0 QUALITY CONTROL

8.1 Each sample should be analyzed twice. If the results do not agree to within 10% expressed as the relative percent difference of the results, repeat the analysis.

8.2 One sample in ten should be spiked with a chlorinated organic at a level of total chlorine commensurate with the levels being determined. The spike recovery should be reported and should be between 80 and 120% of the expected value. Any sample suspected of containing > 25% water should also be spiked with organic chlorine.

9.0 METHOD PERFORMANCE

These data are based on 66 data points obtained by 10 laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate.[1] A data point represents one duplicate analysis of a sample. One laboratory and four additional data points were determined to be outliers and are not included in these results.

9.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method the following values only in 1 case in 20 (see Table 1):

$$\text{Repeatability} = 0.137 \sqrt{x^*}$$

*where x is the average of two results in ug/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$\text{Reproducibility} = 0.455 \sqrt{x^*}$$

*where x is the average value of two results in ug/g.

9.2 Bias. The bias of this test method varies with concentration, as shown in Table 2:

Bias = Amount found - Amount expected

TABLE 1

REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY MICROCOULOMETRIC TITRATION

Average value, ug/g	Repeatability, ug/g	Reproducibility, ug/g
500	69	228
1,000	137	455
1,500	206	683
2,000	274	910
2,500	343	1,138
3,000	411	1,365

TABLE 2

RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY MICROCOULOMETRIC TITRATION

Amount expected, ug/g	Amount found ug/g	Bias, ug/g	Percent bias
320	312	-8	-3
480	443	-37	-8
920	841	-79	-9
1,498	1,483	-15	-1
1,527	1,446	-81	-5
3,029	3,016	-13	0
3,045	2,916	-129	-4

1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA80. July 1988.

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EXHIBIT 2

PETROLEUM RECYCLING CORP
PREQUALIFICATION SURVEY

SAMPLE INFORMATION

GENERATOR: INTERNATIONAL LIGHT METAL APPR#: 38210391
TRANSPORTER: P. R. C. REF#: S1047
SAMPLE ID: 3514 DATE SAMPLED: 03/06/91
WASTE TYPE: WASTE OIL DATE RECEIVED: 03/06/91
SAMPLED BY: JOEY B. DATE OF REPORT: 03/08/91
SUBMITTED BY: JOEY B. ATTN: JOHN C.

LABORATORY REPORT

TEST	RESULT	TEST	RESULT
AQUEOUS COMPONENT %	1.0	LEAD (PPM)	4.3
HYDROCARBON COMPONENT %	98.0	NICKEL (PPM)	0.6
SOLID COMPONENT %	1.0	BERYLLIUM (PPM)	N.D.
PH	7.0	COBALT (PPM)	0.1
COLOR	LT.BROWN	MOLYBDENUM (PPM)	N.D.
ODOR	MILD	VANADIUM (PPM)	0.1
ANTIMONY (PPM)	N.D.	COPPER (PPM)	7.5
ARSENIC (PPM)	N.D.	SILVER (PPM)	0.1
SELENIUM (PPM)	2.4	SILICON (PPM)	0.6
CHROMIUM (PPM)	N.D.	BARIUM (PPM)	42.6
ZINC (PPM)	378.0	CADMIUM (PPM)	0.1
FLASH POINT (PMCC) DEG/F =	200	TX (PPM)	284.0
		PCB (PPM)	<2.0

COMMENTS: ((N.D)) DENOTES NON DETECTED.

CC: Rolodex Card ____
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Cyrus Pourhassanian
Laboratory Manager

Petroleum Recycling Corp.
Plant — 1835 East 29th Street, Signal Hill, California 90806 (213) 595-6597
Office — 2651 Walnut Avenue, Signal Hill, California 90806 (213) 595-7431

EXHIBIT 3

METHOD 8080

ORGANOCHLORINE PESTICIDES AND PCBs

1.0 SCOPE AND APPLICATION

1.1 Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs). Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8080 provides gas chromatographic conditions for the detection of ppb levels of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a halogen-specific detector (HSD).

2.2 The sensitivity of Method 8080 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8080 may also be performed on samples that have undergone cleanup. Method 3620, Florisil Column Cleanup, by itself or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Section 3.5, in particular), 3600, and 8000.

3.2 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

TABLE 1. GAS CHROMATOGRAPHY OF PESTICIDES AND PCBs[a]

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method Detection limit (ug/L)
Aldrin	2.40	4.10	0.004
α-BHC	1.35	1.82	0.003
β-BHC	1.90	1.97	0.006
δ-BHC	2.15	2.20	0.009
γ-BHC (Lindane)	1.70	2.13	0.004
Chlordane (technical)	e	e	0.014
4,4'-DDD	7.83	9.08	0.011
4,4'-DDE	5.13	7.15	0.004
4,4'-DDT	9.40	11.75	0.012
Dieldrin	5.45	7.23	0.002
Endosulfan I	4.50	6.20	0.014
Endosulfan II	8.00	8.28	0.004
Endosulfan sulfate	14.22	10.70	0.066
Endrin	6.55	8.10	0.006
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.003
Heptachlor epoxide	3.50	5.00	0.083
Methoxychlor	18.20	26.60	0.176
Toxaphene	e	e	0.24
PCB-1016	e	e	nd
PCB-1221	e	e	nd
PCB-1232	e	e	nd
PCB-1242	e	e	0.065
PCB-1248	e	e	nd
PCB-1254	e	e	nd
PCB-1260	e	e	nd

[a]U.S. EPA. Method 617. Organochloride Pesticides and PCBs. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

e = Multiple peak response.

nd = not determined.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas Chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 **Columns:**

4.1.2.1 Column 1: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8-m x 4-mm I.D. glass column or equivalent.

4.1.2.2 Column 2: Supelcoport (100/120 mesh) coated with 3% OV-1 in a 1.8-m x 4-mm I.D. glass column or equivalent.

4.1.3 **Detectors:** Electron capture (ECD) or halogen specific (HSD) (i.e., electrolytic conductivity detector).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.2.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.2.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.5 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2-, 10-, and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, toluene, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. A small volume of toluene may be necessary to put some pesticides in solution. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest are prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with pesticide surrogates. Because GC/ECD data are much more subject to interference than GC/MS, a secondary surrogate is to be used when sample interference is apparent. Dibutylchlorendate (DBC) is also subject to acid and base degradation. Therefore, two surrogate standards are added to each sample; however, only one need be calculated for recovery. DBC is the primary surrogate and should be used whenever possible. However, if DBC recovery is low or compounds interfere with DBC, then the 2,4,5,6-tetrachloro-meta-xylene should be evaluated for acceptance. Proceed with corrective action when both surrogates are out of limits for a sample (Section 8.3). Method 3500, Section 5.3.2, indicates the proper procedure for preparing these surrogates.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Increase the temperature of the hot water bath to about 90°C. Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature is set at 200°C isothermal. When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 160°C.

7.2.2 **Column 2:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature held isothermal at 200°C. When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 140°C.

7.2.3 When analyzing for most or all of the analytes in this method, adjust the oven temperature and column gas flow so that 4,4'-DDT has a retention time of approximately 12 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated than the mid-level standard. Inject this prior to beginning initial or daily calibration.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of GC/ECD chromatograms for various pesticides and PCBs are shown in Figures 1 through 5.

7.4.4 Prime the column as per Paragraph 7.3.2.

7.4.5 DDT and endrin are easily degraded in the injection port if the injection port or front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-level standard containing only 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration, by following the GC system maintenance outlined in Section 7.7 of Method 8000. Calculate percent breakdown as follows:

$$\%\ \text{breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100$$

$$\%\ \text{breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{Total endrin peak area (endrin + endrin aldehyde + endrin ketone)}} \times 100$$

7.4.6 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.7 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.4.8 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo cleanup using Method 3620. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove Sulfur using Method 3660.

7.5 Cleanup:

7.5.1 Proceed with Method 3620, followed by, if necessary, Method 3660, using the 10-mL hexane extracts obtained from Paragraph 7.1.2.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

7.6 Calculations (exerpted from U.S. FDA, PAM):

7.6.1 **Calculation of Certain Residues:** Residues which are mixtures of two or more components present problems in measurement. When they are found together, e.g., toxaphene and DDT, the problem of quantitation becomes even more difficult. In the following sections suggestions are offered for handling toxaphene, chlordane, PCB, DDT, and BHC. A column 10% DC-200 stationary phase was used to obtain the chromatograms in Figures 6-9.

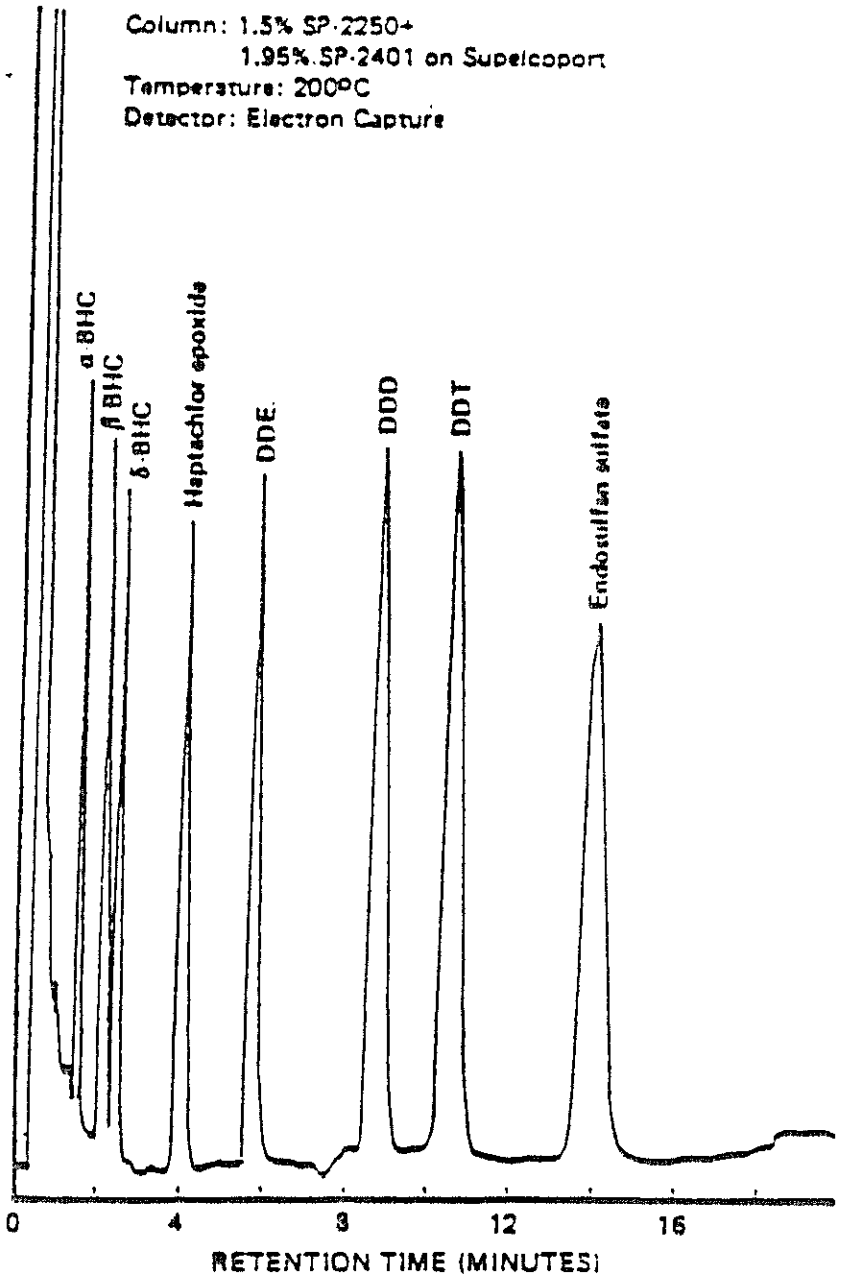

Figure 1. Gas chromatogram of pesticides.

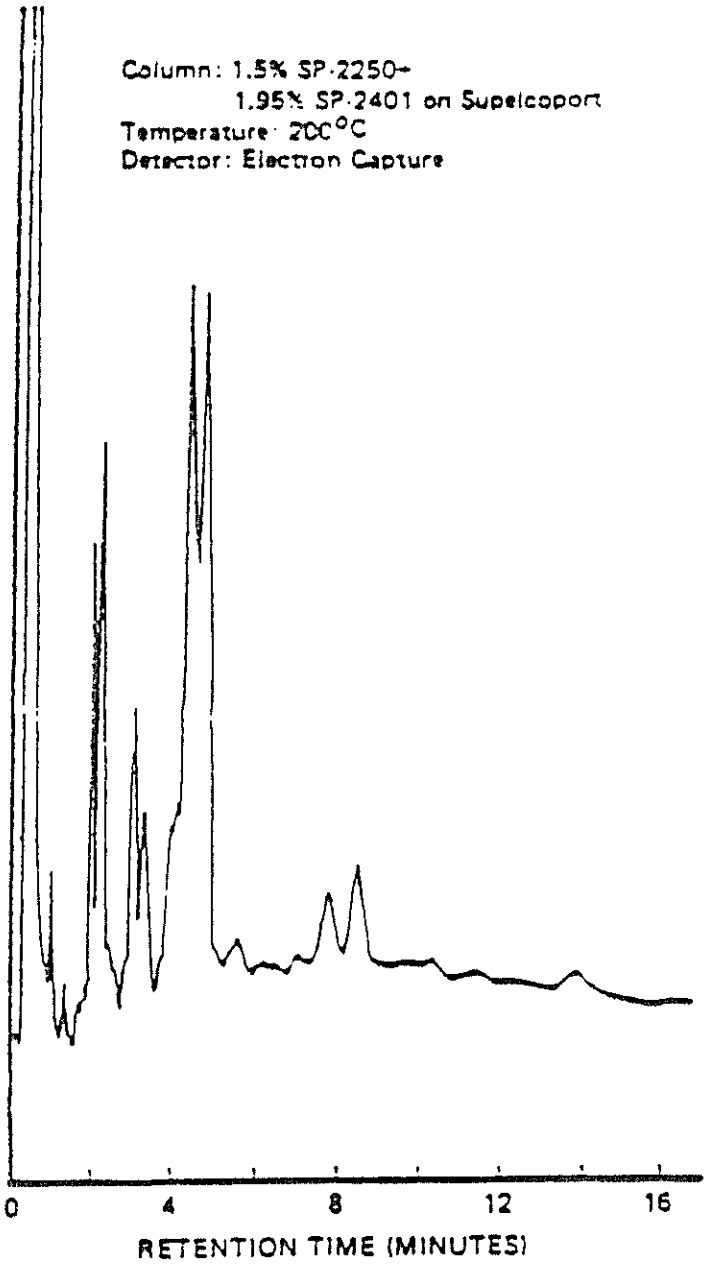

Figure 2. Gas chromatogram of chlordane.

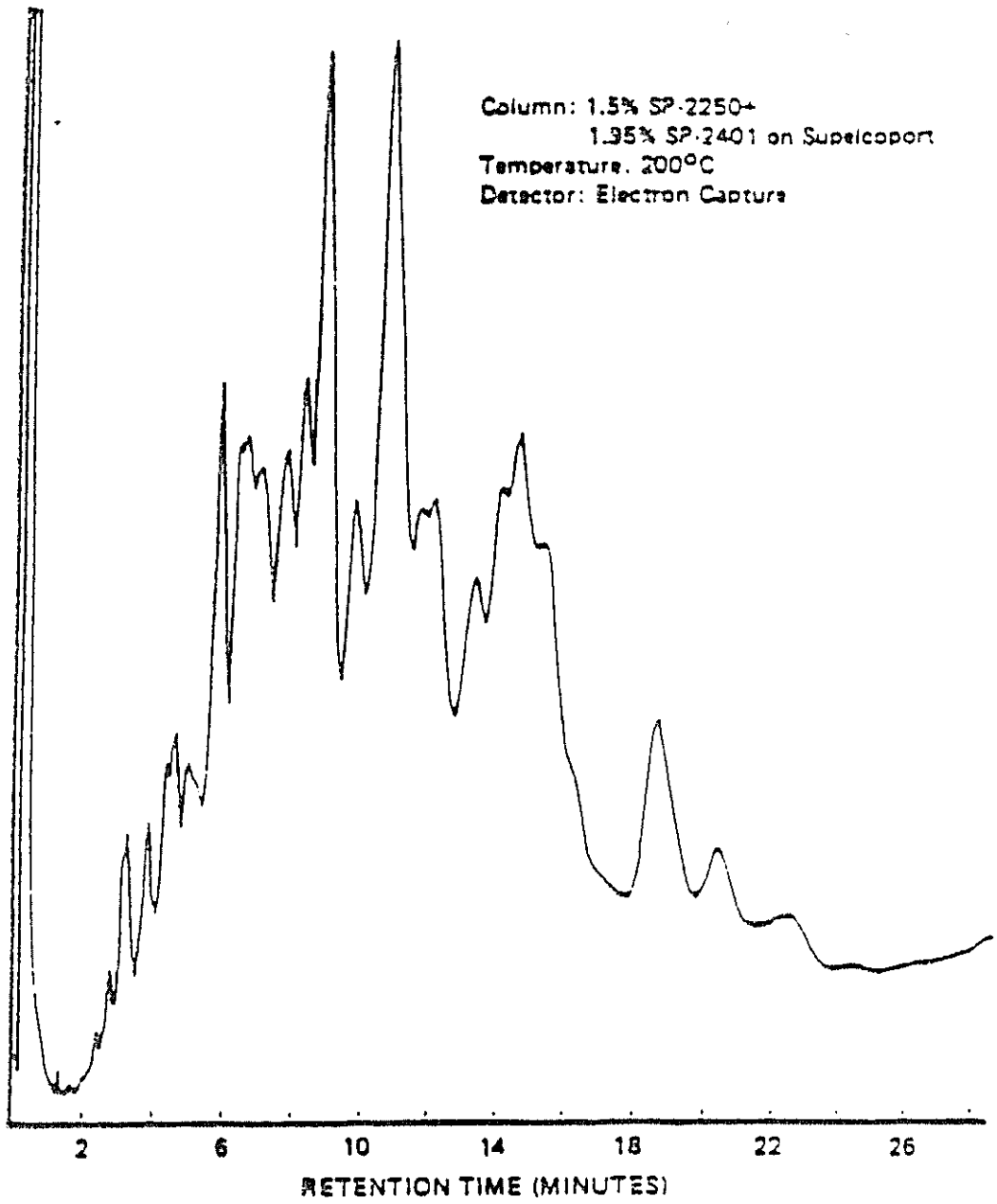

Figure 3. Gas chromatogram of toxaphene.

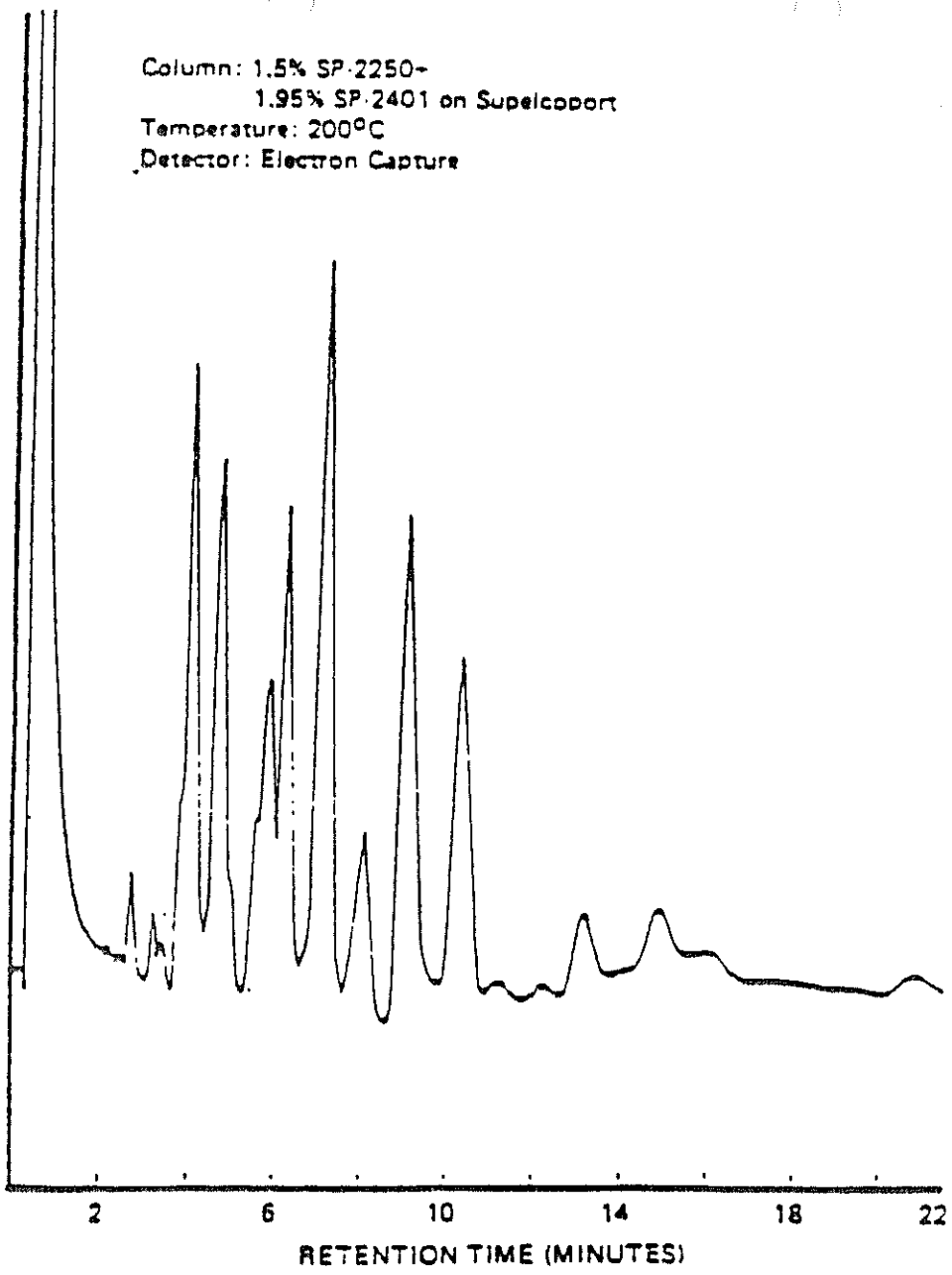

Figure 4. Gas chromatogram of PCB-1254.

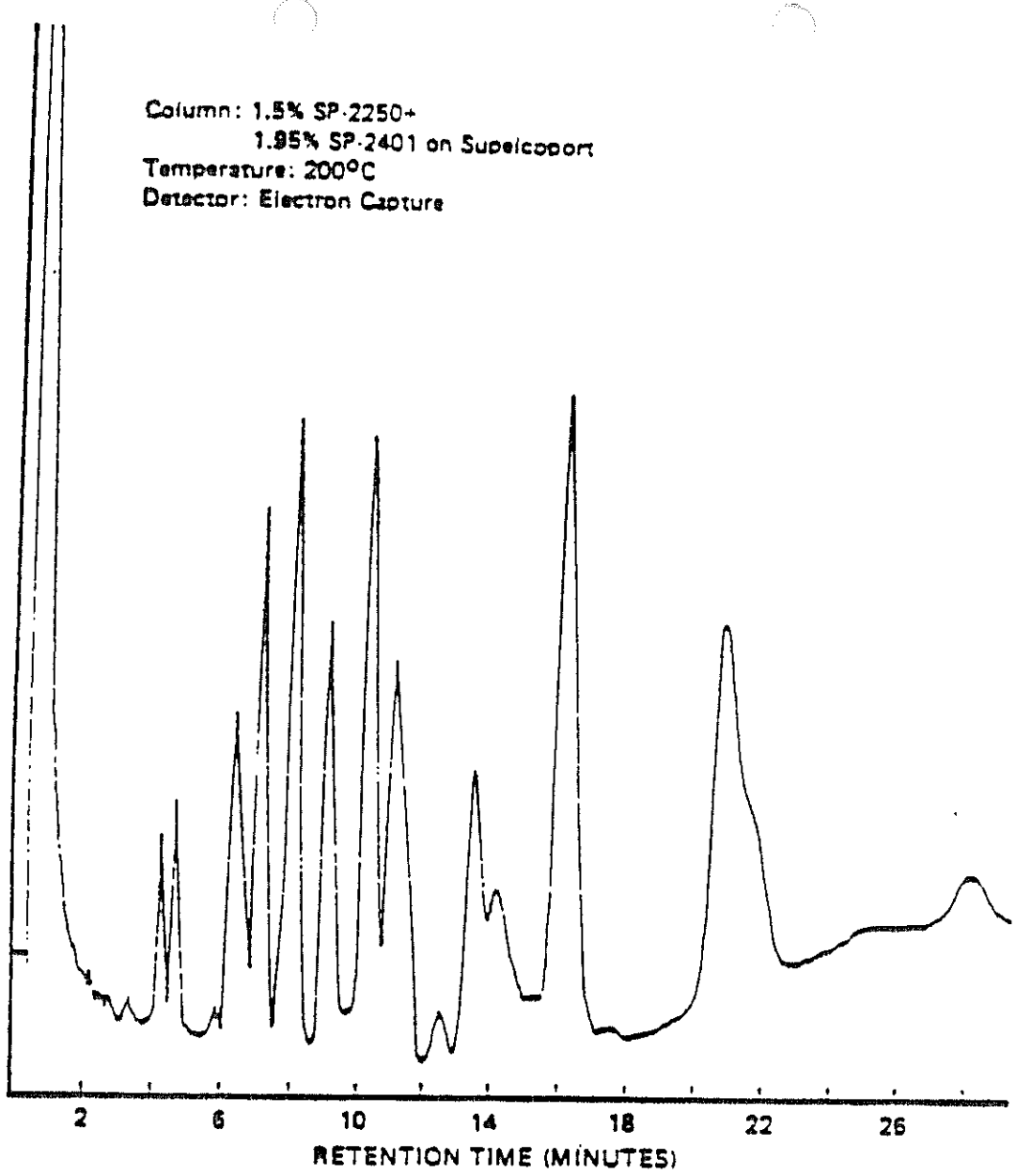

Figure 5. Gas chromatogram of PCB-1260.

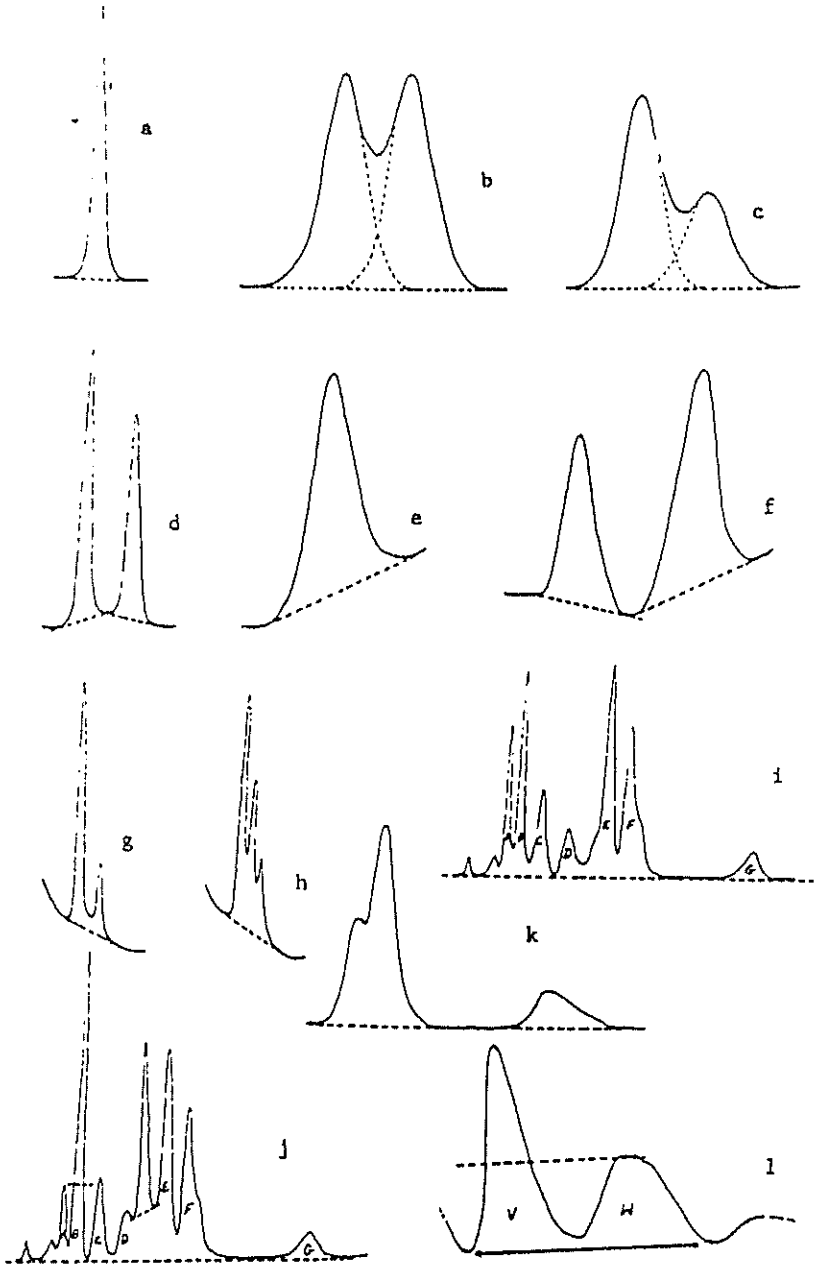

Fig. 6--Baseline construction for some typical gas chromatographic peaks. a, symmetrical separated flat baseline; b and c, overlapping flat baseline; d, separated (pen does not return to baseline between peaks); e, separated sloping baseline; f, separated (pen goes below baseline between peaks); g, α- and γ-BHC sloping baseline; h, α-, β-, and γ-BHC sloping baseline; i, chlordane flat baseline; j, heptachlor and heptachlor epoxide superimposed on chlordane; k, chair-shaped peaks, unsymmetrical peak; l, p,p'-DDT superimposed on toxaphene.

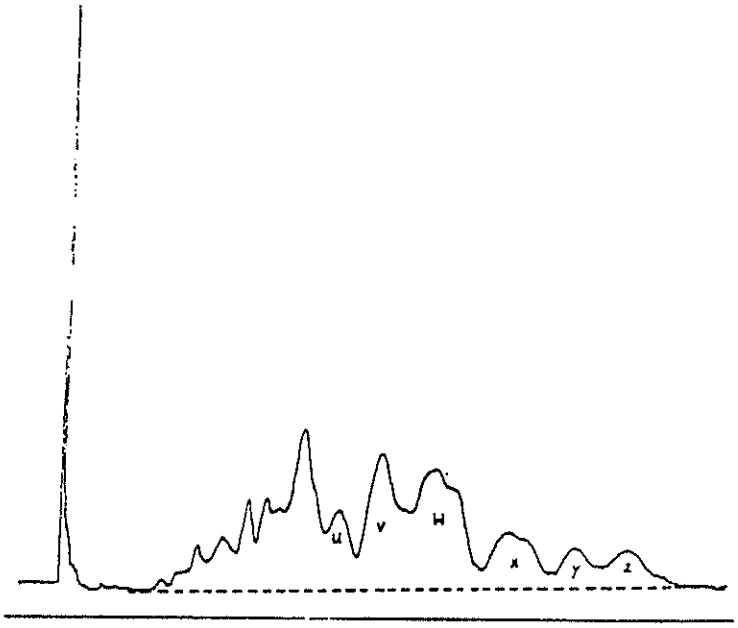

Fig. 7a--Baseline construction for multiple residues with standard toxaphene.

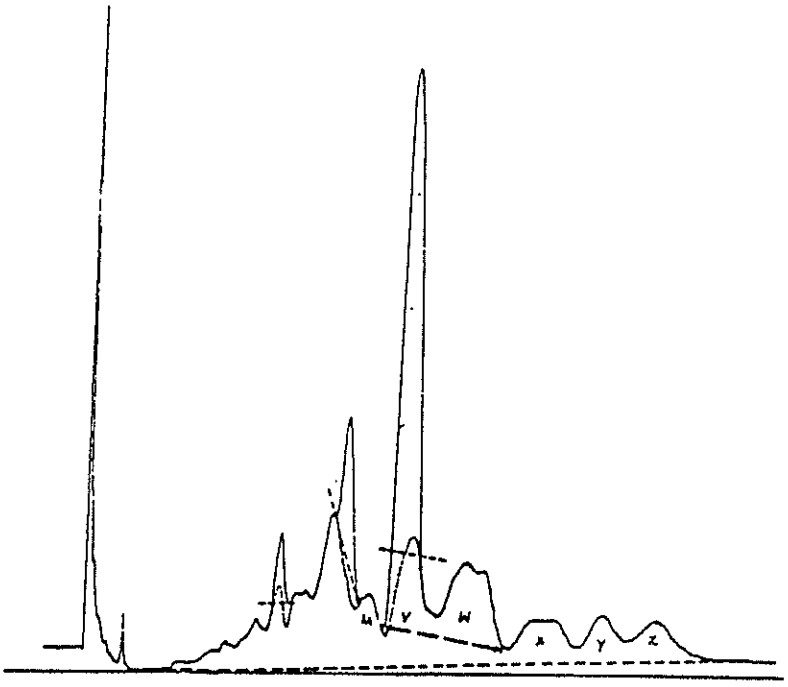

Fig. 7b--Baseline construction for multiple residues with toxaphene, DDE and o,p'-, and p,p'-DDT.

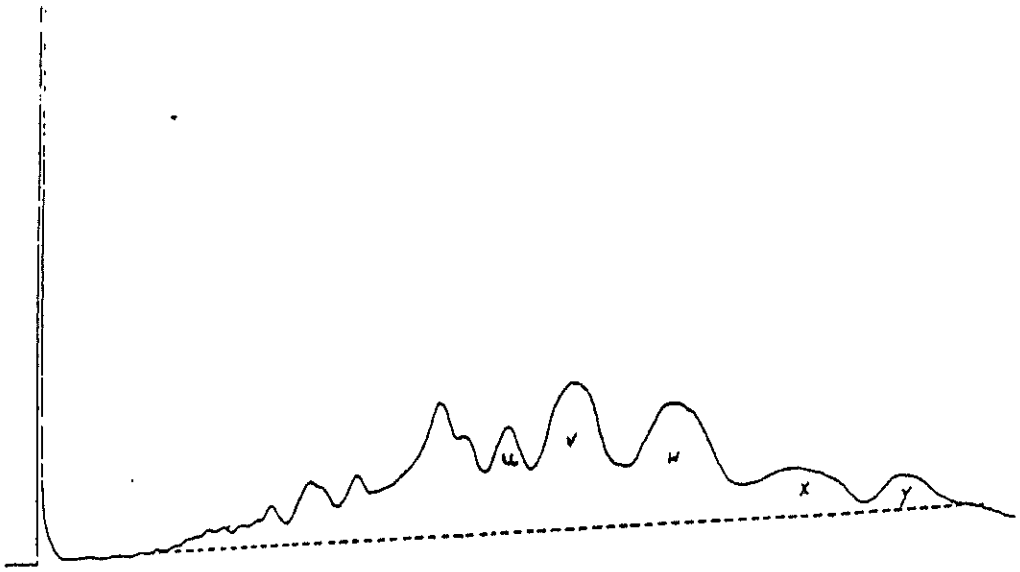

Fig. 8a--Baseline construction for multiple residues: standard toxaphene.

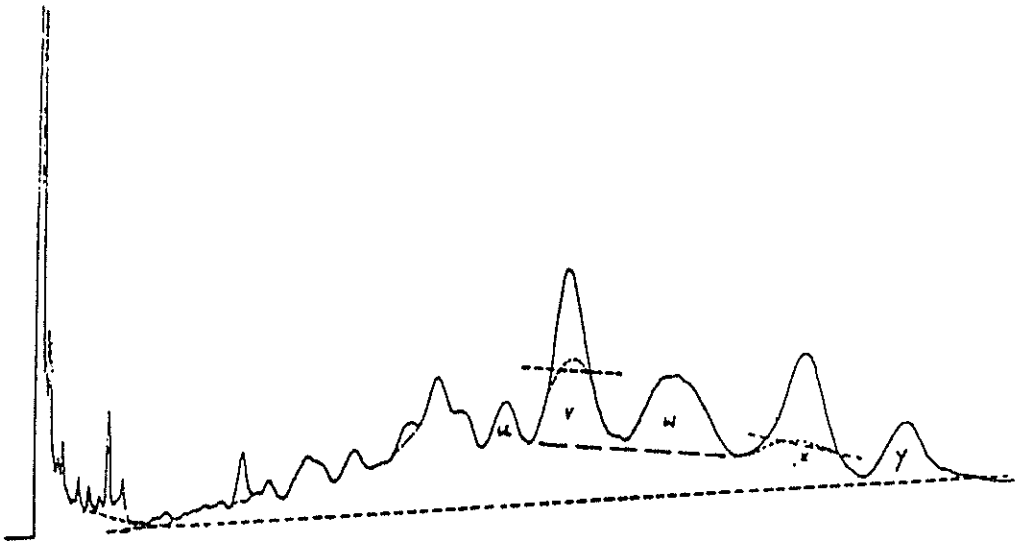

Fig. 8b--Baseline construction for multiple residues: rice bran with BHC, toxaphene, DDT, and methoxychlor.

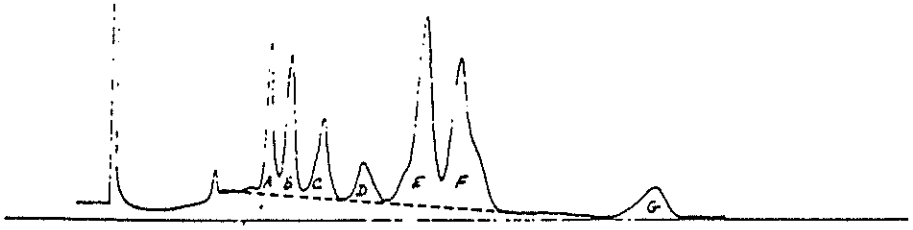

Fig. 9a--Baseline construction for multiple residues: standard chlordane.

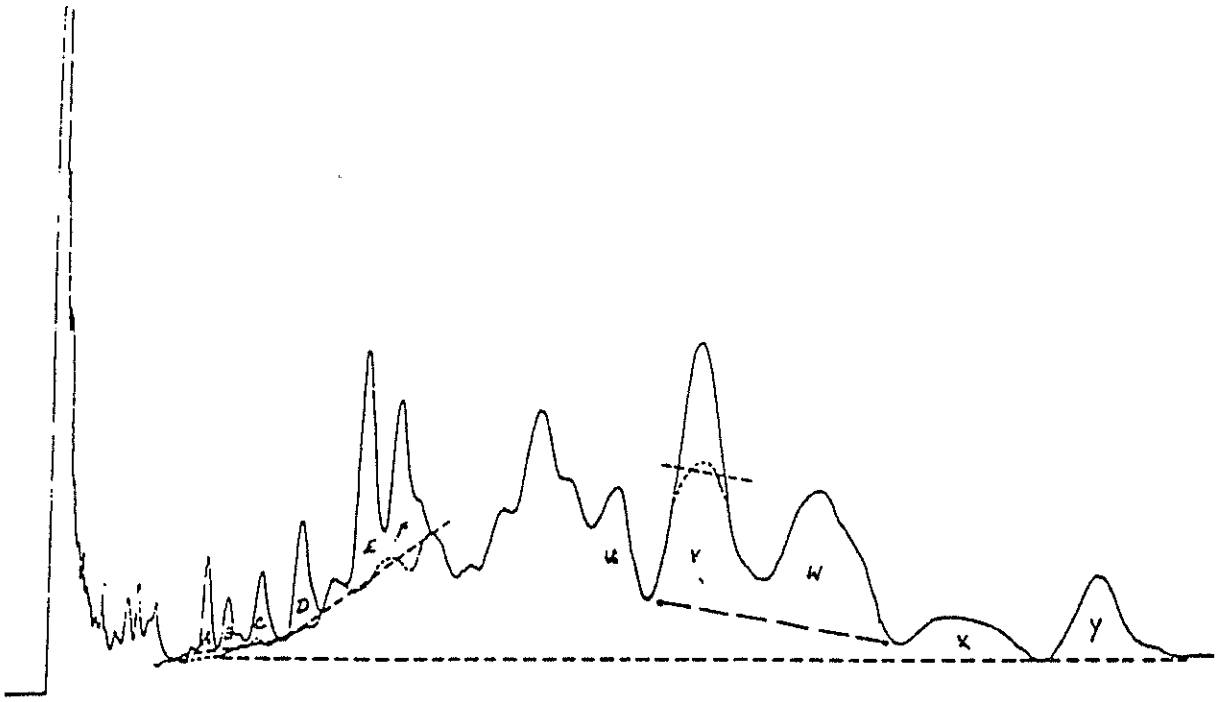

Fig. 9b—Baseline construction for multiple residues: rice bran with chlordane, toxaphene, and DDT.

7.6.2 Toxaphene: Quantitative calculation of toxaphene or Strobane is difficult, but reasonable accuracy can be obtained. To calculate toxaphene on GC/ECD: (a) adjust sample size so that toxaphene major peaks are 10-30% full-scale deflection (FSD); (b) inject a toxaphene standard that is estimated to be within ±10 ng of the sample; (c) construct the baseline of standard toxaphene between it extremities; and (d) construct the baseline under the sample, using the distances of the peak troughs to baseline on the standard as a guide (Figures 7, 8, and 9). This procedure is made difficult by the fact that the relative heights and widths of the peaks in the sample will probably not be identical to the standard. A toxaphene standard that has been passed through a Florisil column will show a shorter retention time for peak X and an enlargement of peak Y.

7.6.3 Toxaphene and DDT: If DDT is present, it will superimpose itself on toxaphene peak V. To determine the approximate baseline of the DDT, draw a line connecting the trough of peaks U and V with the trough of peaks W and X and construct another line parallel to this line which will just cut the top of peak W (Figure 61). This procedure was tested with ratios of standard toxaphene-DDT mixtures from 1:10 to 2:1 and the results of added and calculated DDT and toxaphene by the "parallel lines" method of baseline construction were within 10% of the actual values in all cases.

7.6.3.1 A series of toxaphene residues have been calculated using total peak area for comparison to the standard and also using area of the last four peaks only in both sample and standard. The agreement between the results obtained by the two methods justifies the use of the latter method for calculating toxaphene in a sample where the early eluting portion of the toxaphene chromatogram is interfered with by other substances.

7.6.3.2 The baseline for methoxychlor superimposed on toxaphene (Figure 8b) was constructed by overlaying the samples on a toxaphene standard of approximately the same concentration (Figure 8a) and viewing the charts against a lighted background.

7.6.4 Chlordane is a technical mixture of at least 11 major components and 30 or more minor ones. Gas chromatography-mass spectrometry and nuclear magnetic resonance analytical techniques have been applied to the elucidation of the chemical structures of the many chlordane constituents. Figure 9a is a chromatogram of standard chlordane. Peaks E and F are responses to trans- and cis-chlordane, respectively. These are the two major components of technical chlordane, but the exact percentage of each in the technical material is not completely defined and is not consistent from batch to batch. Other labelled peaks in Figure 9a are thought to represent: A, monochlorinated adduct of pentachlorocyclopentadiene with cyclopentadiene; B, coelution of heptachlor and α-chlordene; C, coelution of β-chlordene and γ-chlordene;

D, a chlordane analog; G, coelution of cis-nonachlor and "Compound K," a chlordane isomer. The right "shoulder" of peak F is caused by trans-nonachlor.

7.6.4.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of: constituents from the technical chlordane; plant and/or animal metabolities; and products of degradation caused by exposure to environmental factors such as water and sunlight. Only limited information is available on which residue GC patterns are likely to occur in which samples types, and even this information may not be applicable to a situation where the route of exposure is unusual. For example, fish exposed to a recent spill of technical chlordane will contain a residue drastically different from a fish whose chlordane residue was accumulated by ingestion of smaller fish or of vegetation, which in turn had accumulated residues because chlordane was in the water from agricultural runoff.

7.6.4.2 Because of this inability to predict a chlordane residue GC pattern, it is not possible to prescribe a single method for the quantitation of chlordane residues. The analyst must judge whether or not the residue's GC pattern is sufficiently similar to that of a technical chlordane reference material to use the latter as a reference standard for quantitation.

7.6.4.3 When the chlordane residue does not resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate each peak separately against the appropriate reference materials and report the individual residues. (Reference materials are available for at least 11 chlordane constituents, metabolites or degradation products which may occur in the residue.)

7.6.4.4 When the GC pattern of the residue resembles that of technical chlordane, quantitate chlordane residues by comparing the total area of the chlordane chromatogram from peaks A through F (Figure 9a) in the sample versus the same part of the standard chromatogram. Peak G may be obscured in a sample by the presence of other pesticides. If G is not obscured, include it in the measurement for both standard and sample. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion as in Figure 6j, calculate these separately and subtract their areas from total area to give a corrected chlordane area. (Note that octachlor epoxide, metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.4.5 To measure the total area of the chlordane chromatogram, proceed as in Section 7.6.2 on toxaphene. Inject an amount of technical chlordane standard which will produce a chromatogram in which peaks E and F are approximately the same size as those in the sample chromatograms. Construct the baseline beneath the standard from the beginning of peak A to the end of peak F as shown in Figure 9a. Use the distance from the trough between peaks E and F to the baseline in the chromatogram of the standard to construct the baseline in the chromatogram of the sample. Figure 9b shows how the presence of toxaphene causes the baseline under chlordane to take an upward angle. When the size of peaks E and F in standard and sample chromatograms are the same, the distance from the trough of the peaks to the baselines should be the same. Measurement of chlordane area should be done by total peak area if possible.

NOTE: A comparison has been made of the total peak area integration method and the addition of peak heights method for several samples containing chlordane. The peak heights A, B, C, D, E, and F were measured in millimeters from peak maximum of each to the baseline constructed under the total chlordane area and were then added together. These results obtained by the two techniques are too close to ignore this method of "peak height addition" as a means of calculating chlordane. The technique has inherent difficulties because not all the peaks are symmetrical and not all are present in the same ratio in standard and in sample. This method does offer a means of calculating results if no means of measuring total area is practical.

7.6.5 **Polychlorinated biphenyls (PCBs):** Quantitation of residues of PCB involves problems similar to those encountered in the quantitation of toxaphene, Strobane, and chlordane: in each case, the chemical is made up of numerous compounds and so the chromatograms are multi-peak; also in each case the chromatogram of the residue may not match that of the standard.

7.6.5.1 Mixtures of PCB of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the tradename Aroclor (1200 series and 1016). Though these Aroclors are no longer marketed, the PCBs remain in the environment and are sometime found as residues in foods, especially fish.

7.6.5.2 PCB residues are quantitated by comparison to one or more of the Aroclor materials, depending on the chromatographic pattern of the residue. A choice must be made as to which Aroclor or mixture of Aroclors will produce a chromatogram most similar to that of the residue. This may also involve a judgment about what proportion of the different Aroclors to combine to produce the appropriate reference material.

7.6.5.3 Quantitate PCB residues by comparing total area or height of residue peaks to total area of height of peaks from appropriate Aroclor(s) reference materials. Measure total area or height response from common baseline under all peaks. Use only those peaks from sample that can be attributed to chlorobiphenyls. These peaks must also be present in chromatogram of reference materials. Mixture of Aroclors may be required to provide best match of GC patterns of sample and reference.

7.6.6 DDT: DDT found in samples often consists of both o,p'- and p,p'-DDT. Residues of DDE and TDE are also frequently present. Each isomer of DDT and its metabolites should be quantitated using the pure standard of that compound and reported as such.

7.6.7 **Hexachlorocyclohexane (BHC, from the former name, benzene hexachloride):** Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachloro-cyclohexanes and octachloro-cyclohexanes.

7.6.7.1 Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. The elimination rate of the isomers fed to rats was 3 weeks for the α-, γ-, and δ-isomers and 14 weeks for the β-isomer. Thus it may be possible to have any combination of the various isomers in different food commodities. BHC found in dairy products usually has a large percentage of β-isomer.

7.6.7.2 Individual isomers (α, β, γ, and δ) were injected into gas chromatographs equipped with flame ionization, microcoulometric, and electron capture detectors. Response for the four isomers is very nearly the same whether flame ionization or microcoulometric GLC is used. The α-, γ-, and δ-isomers show equal electron affinity. β-BHC shows a much weaker electron affinity compared to the others isomers.

7.6.7.3 Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer, using a GC column which separates all the isomers from one another.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Mandatory quality control to evaluate the GC system operation is found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each single-component parameter of interest at the following concentrations in acetone: 4,4'-DDD, 10 ug/mL; 4,4'-DDT, 10 ug/mL; endosulfan II, 10 ug/mL; endosulfan sulfate, 10 ug/mL; endrin, 10ug/mL; and any other single-component pesticide, 2 ug/mL. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multi-component parameter at a concentration of 50 ug/mL in acetone.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 GC/MS confirmation: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits.

8.4.1 The GC/MS would normally require a minimum concentration of 10 ng/uL in the final extract, for each single-component compound.

8.4.2 The pesticide extract and associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270.

8.4.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extractables extracts (sample and blank). However, if the compounds are not detected in the base/neutral-acid extract even though the concentration is high enough, a GC/MS analysis of the pesticide extract should be performed.

8.4.4 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the pesticides/PCBs identified by GC/ECD.

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations. Concentrations used in the study ranged from 0.5 to 30 ug/L for single-component pesticides and from 8.5 to 400 ug/L for multi-component parameters. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, optional cleanup techniques, and calibration procedures used.

10.0 REFERENCES

1. U.S. EPA, "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 10: Pesticides and PCBs," Report for EPA Contract 68-03-2605.

2. U.S. EPA, "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, October 1980.

3. Pressley, T.A., and J.E. Longbottom, "The Determination of Organohalide Pesticides and PCBs in Industrial and Municipal Wastewater: Method 617," U.S. EPA/EMSL, Cincinnati, OH, EPA-600/4-84-006, 1982.

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5. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9, 1971.

6. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

7. Webb, R.G. and A.C. McCall, "Quantitative PCB Standards for Electron Capture Gas Chromatography," Journal of Chromatographic Science, 11, 366, 1973.

8. Millar, J.D., R.E. Thomas and H.J. Schattenberg, "EPA Method Study 18, Method 608: Organochlorine Pesticides and PCBs," U.S. EPA/EMSL, Research Triangle Park, NC, EPA-600/4-84-061, 1984.

9. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

10. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

11. U.S. Food and Drug Administration, Pesticide Analytical Manual, Vol. 1, June 1979.

12. Sawyer, L.D., JAOAC, 56, 1015-1023 (1973), 61 272-281 (1978), 61 282-291 (1978).

13. Official Methods of Analysis of the Association of Official Analytical Chemists, 12th Edition; Changes in Methods, JAOAC 61, 465-466 (1978), Sec. 29.018.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_S (%)
Aldrin	2.0	0.42	1.08-2.24	42-122
α-BHC	2.0	0.48	.98-2.44	37-134
β-BHC	2.0	0.64	0.78-2.60	17-147
δ-BHC	2.0	0.72	1.01-2.37	19-140
γ-BHC	2.0	0.46	0.86-2.32	32-127
Chlordane	50	10.0	27.6-54.3	45-119
4,4'-DDD	10	2.8	4.8-12.6	31-141
4,4'-DDE	2.0	0.55	1.08-2.60	30-145
4,4'-DDT	10	3.6	4.6-13.7	25-160
Dieldrin	2.0	0.76	1.15-2.49	36-146
Endosulfan I	2.0	0.49	1.14-2.82	45-153
Endosulfan II	10	6.1	2.2-17.1	D-202
Endosulfan Sulfate	10	2.7	3.8-13.2	26-144
Endrin	10	3.7	5.1-12.6	30-147
Heptachlor	2.0	0.40	0.86-2.00	34-111
Heptachlor epoxide	2.0	0.41	1.13-2.63	37-142
Toxaphene	50	12.7	27.8-55.6	41-126
PCB-1016	50	10.0	30.5-51.5	50-114
PCB-1221	50	24.4	22.1-75.2	15-178
PCB-1232	50	17.9	14.0-98.5	10-215
PCB-1242	50	12.2	24.8-69.6	39-150
PCB-1248	50	15.9	29.0-70.2	38-158
PCB-1254	50	13.8	22.2-57.9	29-131
PCB-1260	50	10.4	18.7-54.9	8-127

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_S = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 608. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Aldrin	0.81C+0.04	0.16$\bar{X}$-0.04	0.20$\bar{X}$-0.01
α-BHC	0.84C+0.03	0.13$\bar{X}$+0.04	0.23$\bar{X}$-0.00
β-BHC	0.81C+0.07	0.22$\bar{X}$+0.02	0.33$\bar{X}$-0.95
δ-BHC	0.81C+0.07	0.18$\bar{X}$+0.09	0.25$\bar{X}$+0.03
γ-BHC	0.82C-0.05	0.12$\bar{X}$+0.06	0.22$\bar{X}$+0.04
Chlordane	0.82C-0.04	0.13$\bar{X}$+0.13	0.18$\bar{X}$+0.18
4,4'-DDD	0.84C+0.30	0.20$\bar{X}$-0.18	0.27$\bar{X}$-0.14
4,4'-DDE	0.85C+0.14	0.13$\bar{X}$+0.06	0.28$\bar{X}$-0.09
4,4'-DDT	0.93C-0.13	0.17$\bar{X}$+0.39	0.31$\bar{X}$-0.21
Dieldrin	0.90C+0.02	0.12$\bar{X}$+0.19	0.16$\bar{X}$+0.16
Endosulfan I	0.97C+0.04	0.10$\bar{X}$+0.07	0.18$\bar{X}$+0.08
Endosulfan II	0.93C+0.34	0.41$\bar{X}$-0.65	0.47$\bar{X}$-0.20
Endosulfan Sulfate	0.89C-0.37	0.13$\bar{X}$+0.33	0.24$\bar{X}$+0.35
Endrin	0.89C-0.04	0.20$\bar{X}$+0.25	0.24$\bar{X}$+0.25
Heptachlor	0.69C+0.04	0.06$\bar{X}$+0.13	0.16$\bar{X}$+0.08
Heptachlor epoxide	0.89C+0.10	0.18$\bar{X}$-0.11	0.25$\bar{X}$-0.08
Toxaphene	0.80C+1.74	0.09$\bar{X}$+3.20	0.20$\bar{X}$+0.22
PCB-1016	0.81C+0.50	0.13$\bar{X}$+0.15	0.15$\bar{X}$+0.45
PCB-1221	0.96C+0.65	0.29$\bar{X}$-0.76	0.35$\bar{X}$-0.62
PCB-1232	0.91C+10.79	0.21$\bar{X}$-1.93	0.31$\bar{X}$+3.50
PCB-1242	0.93C+0.70	0.11$\bar{X}$+1.40	0.21$\bar{X}$+1.52
PCB-1248	0.97C+1.06	0.17$\bar{X}$+0.41	0.25$\bar{X}$-0.37
PCB-1254	0.76C+2.07	0.15$\bar{X}$+1.66	0.17$\bar{X}$+3.62
PCB-1260	0.66C+3.76	0.22$\bar{X}$-2.37	0.39$\bar{X}$-4.86

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

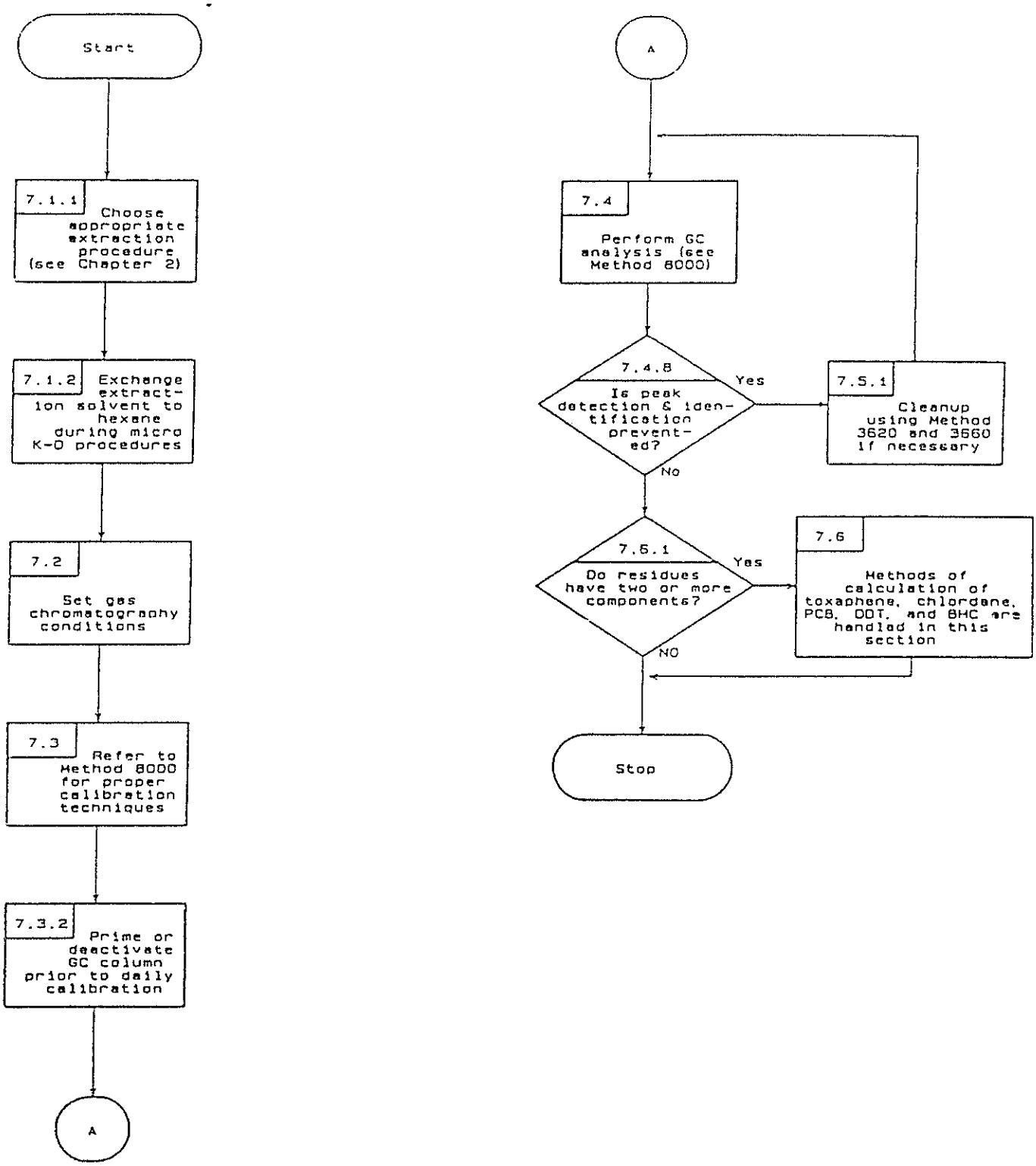

Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during micro K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Prime or deactivate GC column prior to daily calibration
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.8 Is peak detection & identification prevented?
Yes
7.5.1 Cleanup using Method 3620 and 3660 if necessary
No
7.6.1 Do residues have two or more components?
Yes
7.6 Methods of calculation of toxaphene, chlordane, PCB, DDT, and BHC are handled in this section
NO
Stop

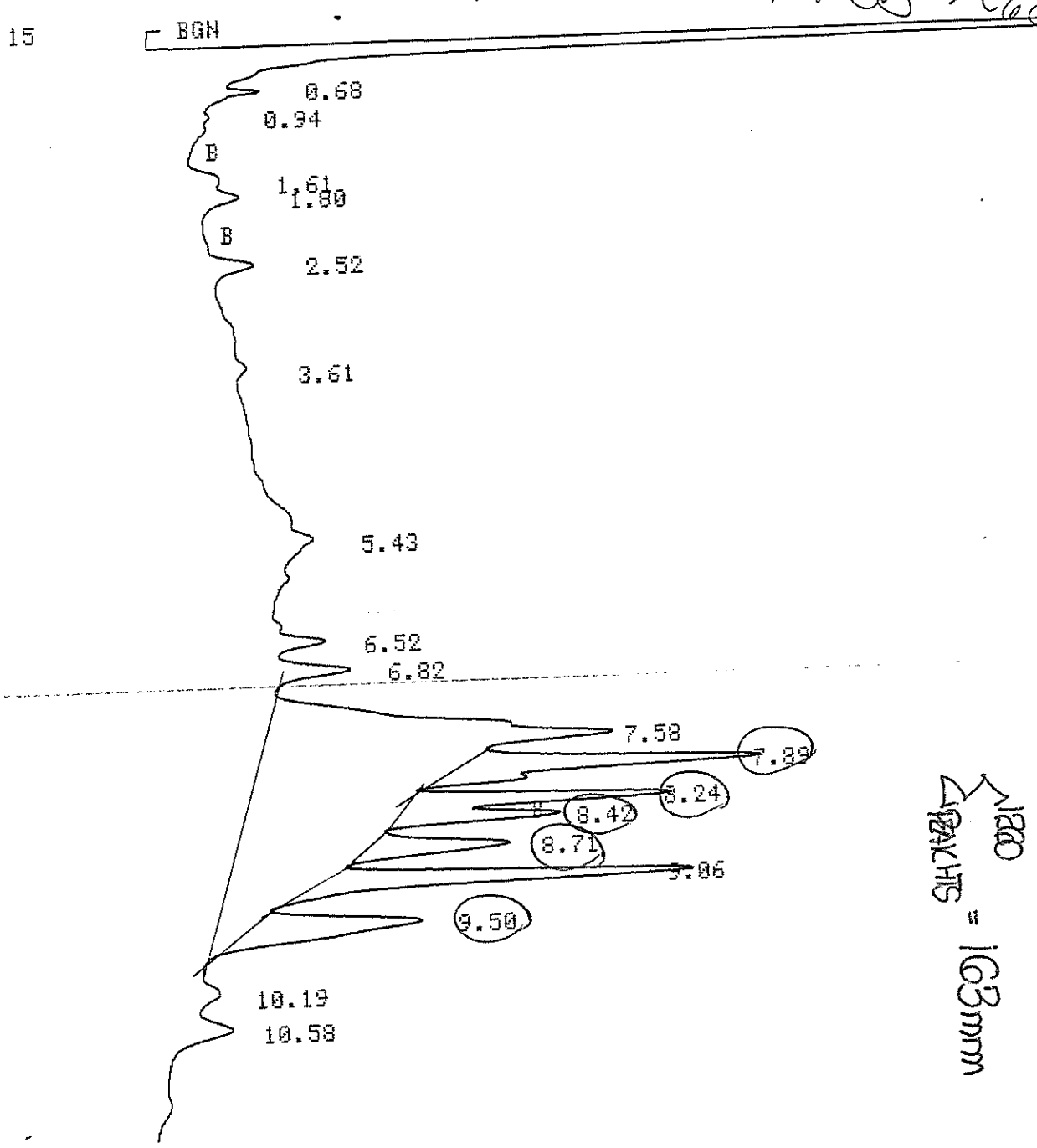
EXHIBIT 4

5 4:32 91/03/12

5 PCB

1µl. 0.5ppm PCB 1260

15 BGN

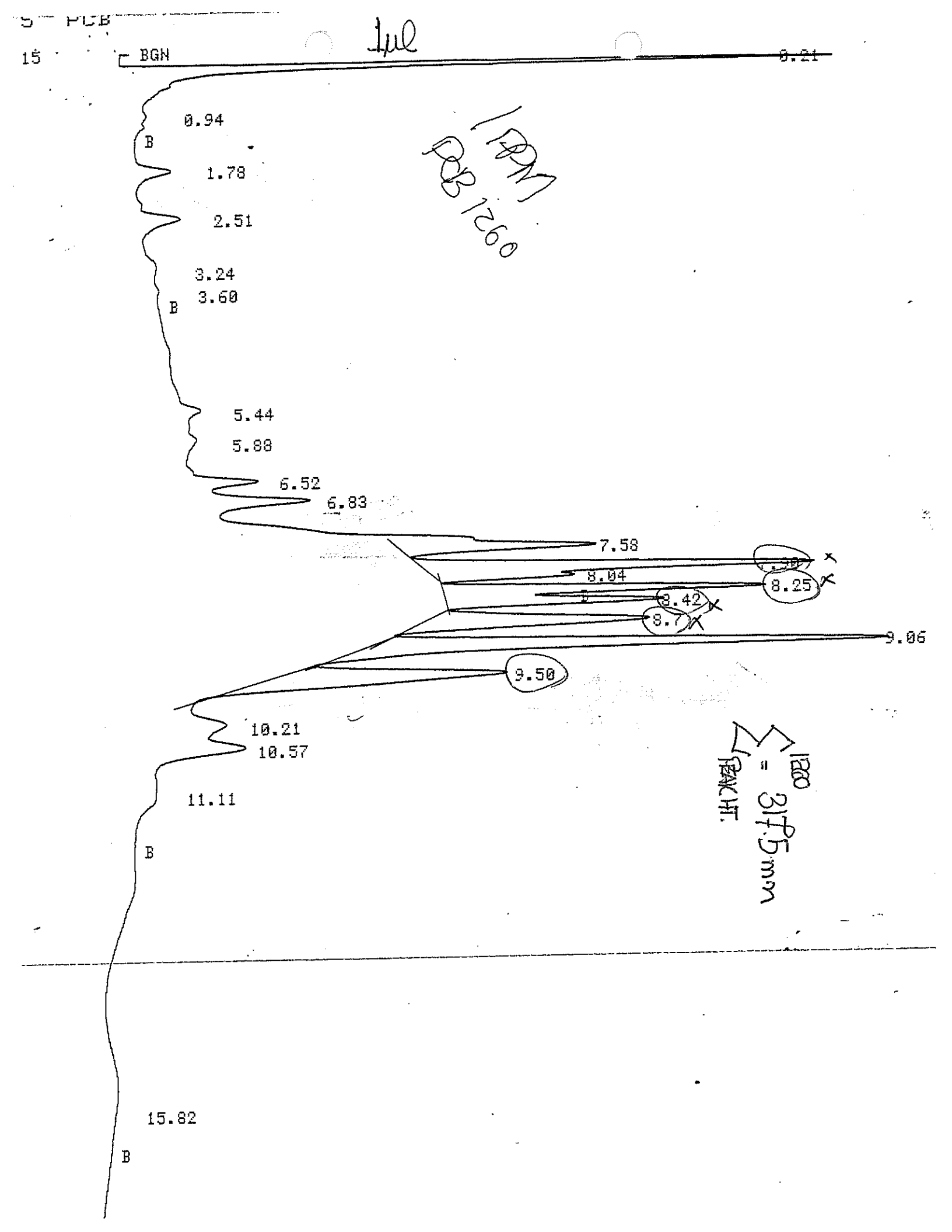


1µl 0.5ppm PCB 1260 = 125pg on column

RUN 5 4:32 91/03/12

METHOD 5 PCB CALCULATION: %

RT	AREA	BC	AREA %
0.24	124.7795	T	34.0791
0.68	8.4388	T	2.3047
0.94	4.8266		1.3182
1.61	2.6963	T	0.7364
1.80	4.1649		1.1375
2.52	4.0321	V	1.1012
	0.7434	V	0.2030


5 PCB
15
BGN
1µl
0.21
0.94
B
1.78
2.51
3.24
3.60
B
5.44
5.88
6.52
6.83
7.58
8.04
8.25
8.42
8.7
9.06
9.50
10.21
10.57
11.11
B
15.82
B
1PPM PCB 1260
1260 = 3175.mm PEAK HT.

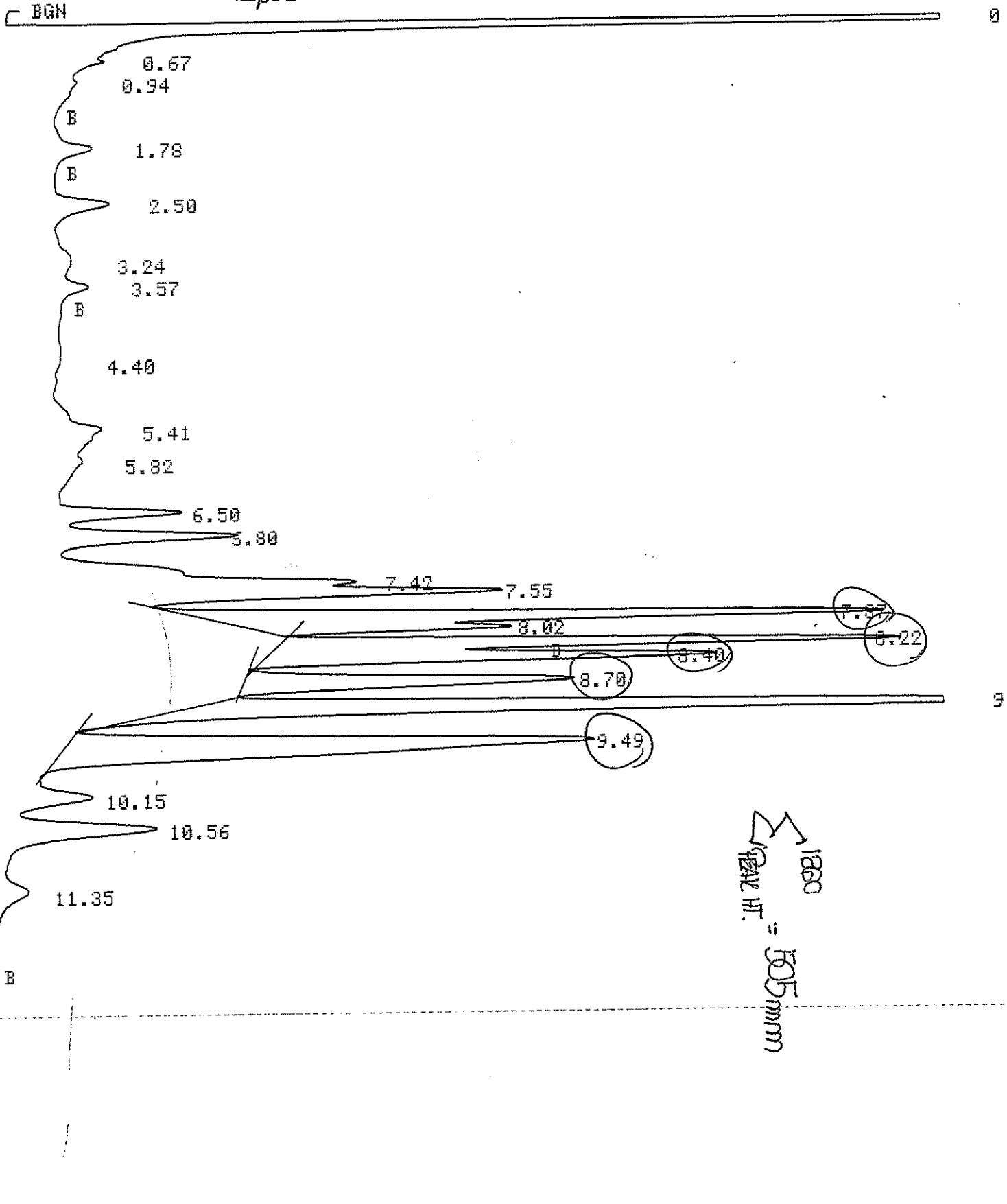
19 PEAKS . > AREA/HT REJECT

7ppm PCB 1260

4:46 91/03/12

PCB

1µl



9.50	3.3907	V	0.7988
10.60	6.3725		0.1791

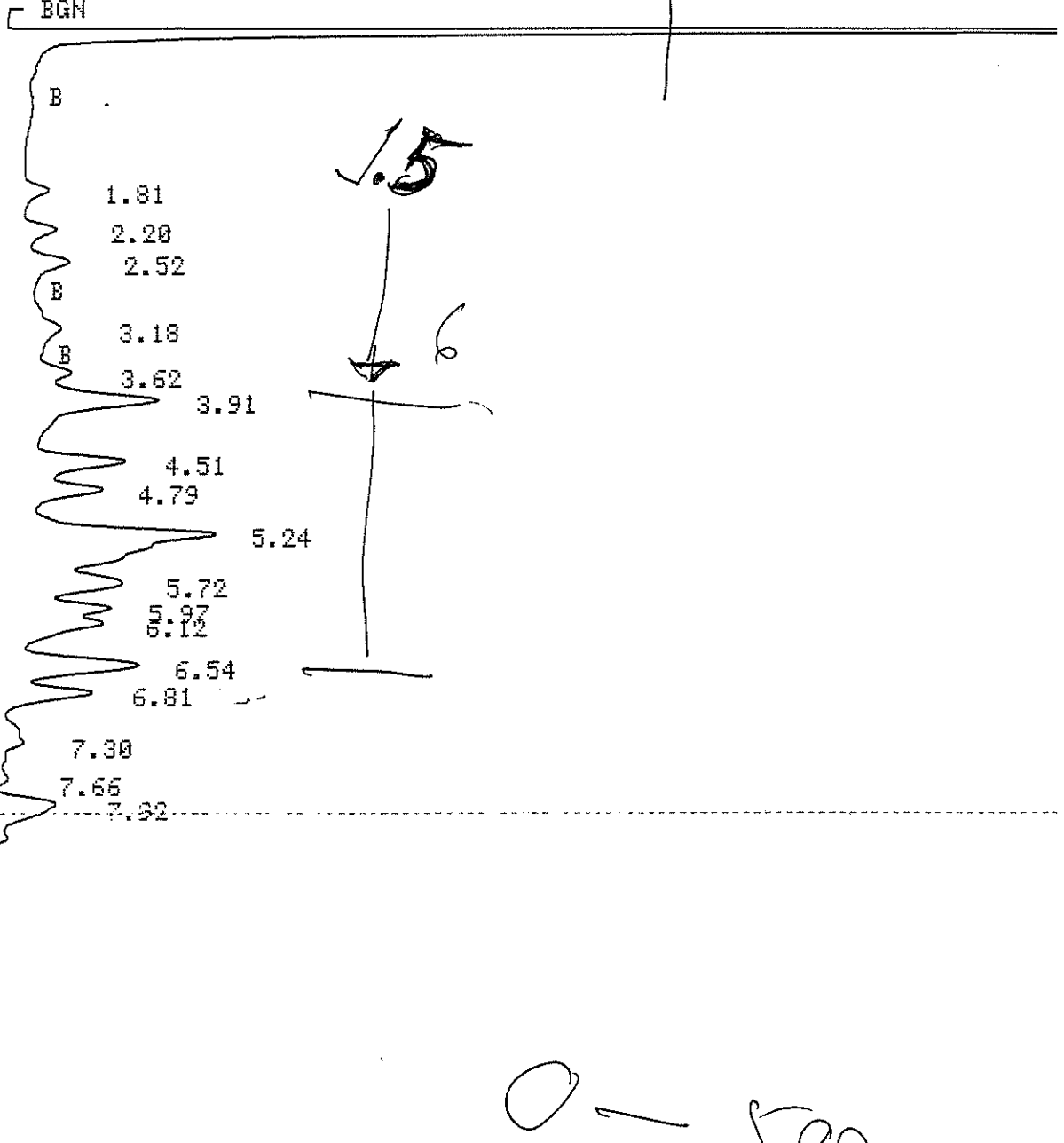
23 PEAKS > AREA/HT REJECT

1µl PCB 1232 1ppm

RUN 16 7:45 91/03/12

METHOD 5 PCB

A 64 C 15



7.92 14.3058 6.6797

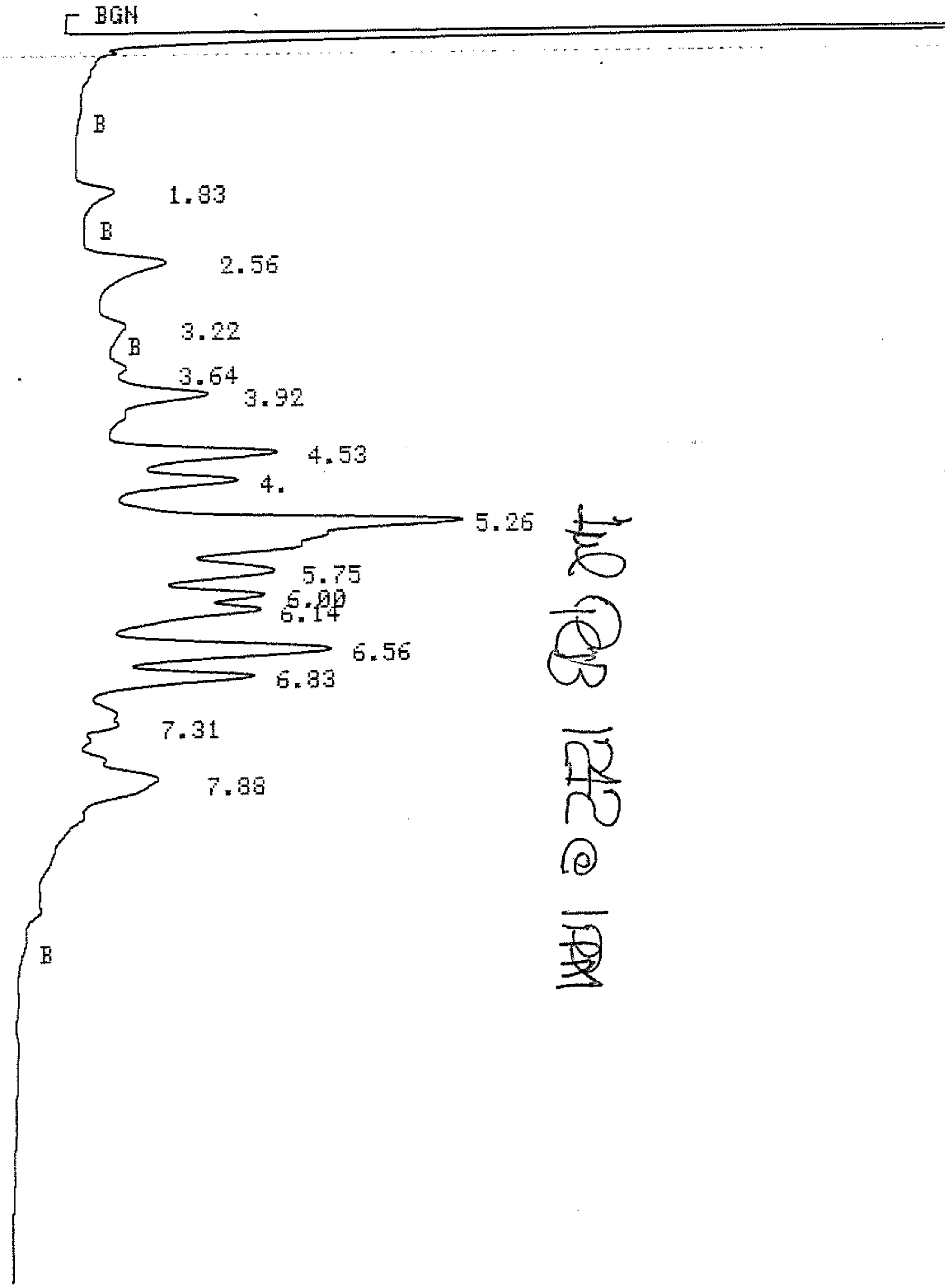
18 PEAKS > AREA/HT REJECT

RUN 17 8:03 91/03/12

METHOD 5 PCB

A 64 C 15

W 6



W 7

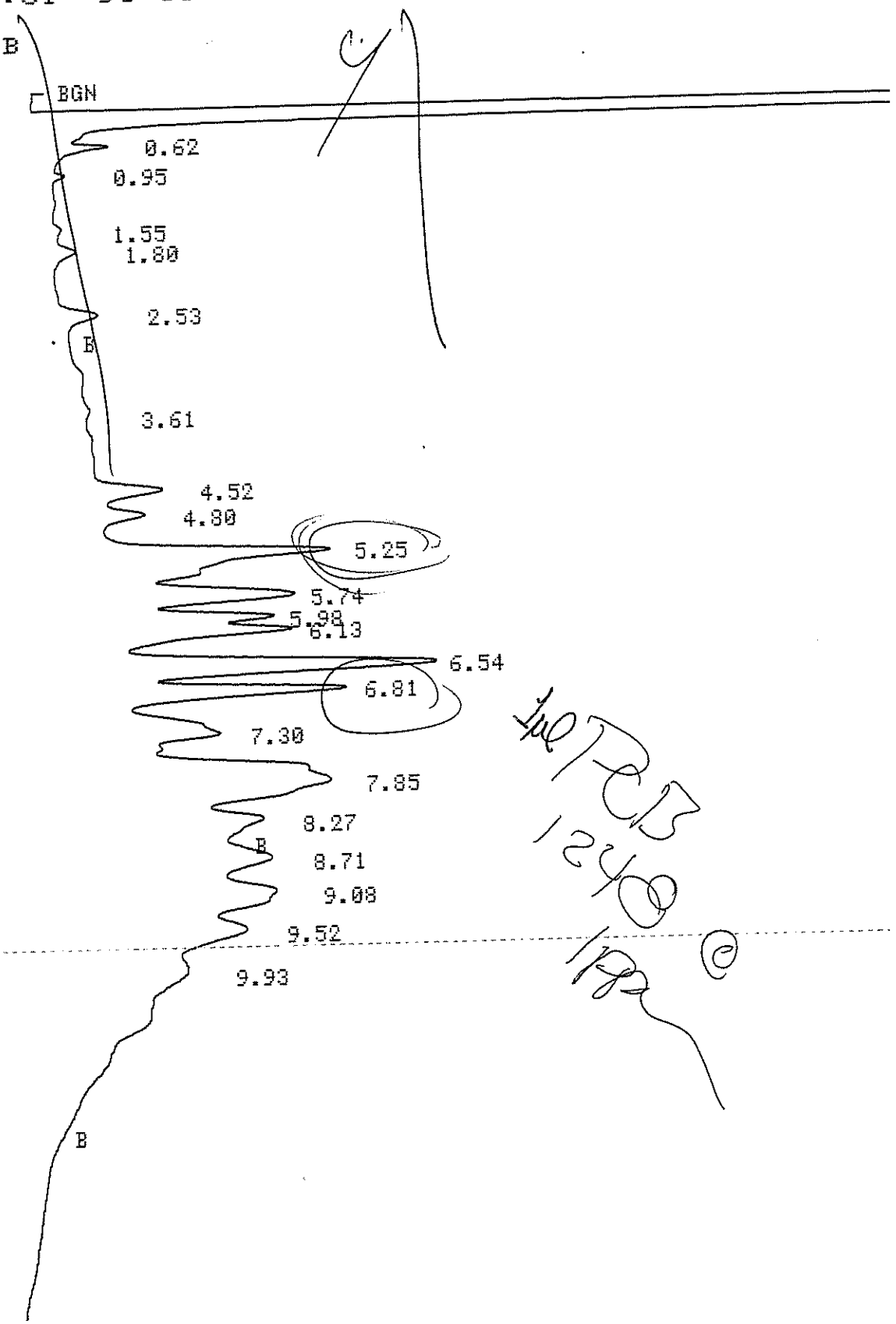
RUN 17 8:03 91/03/12

METHOD 5 PCB CALCULATION: %

RUN 22 10:51 91/03/12

METHOD 5 PCB

A 64 C 15



W 6

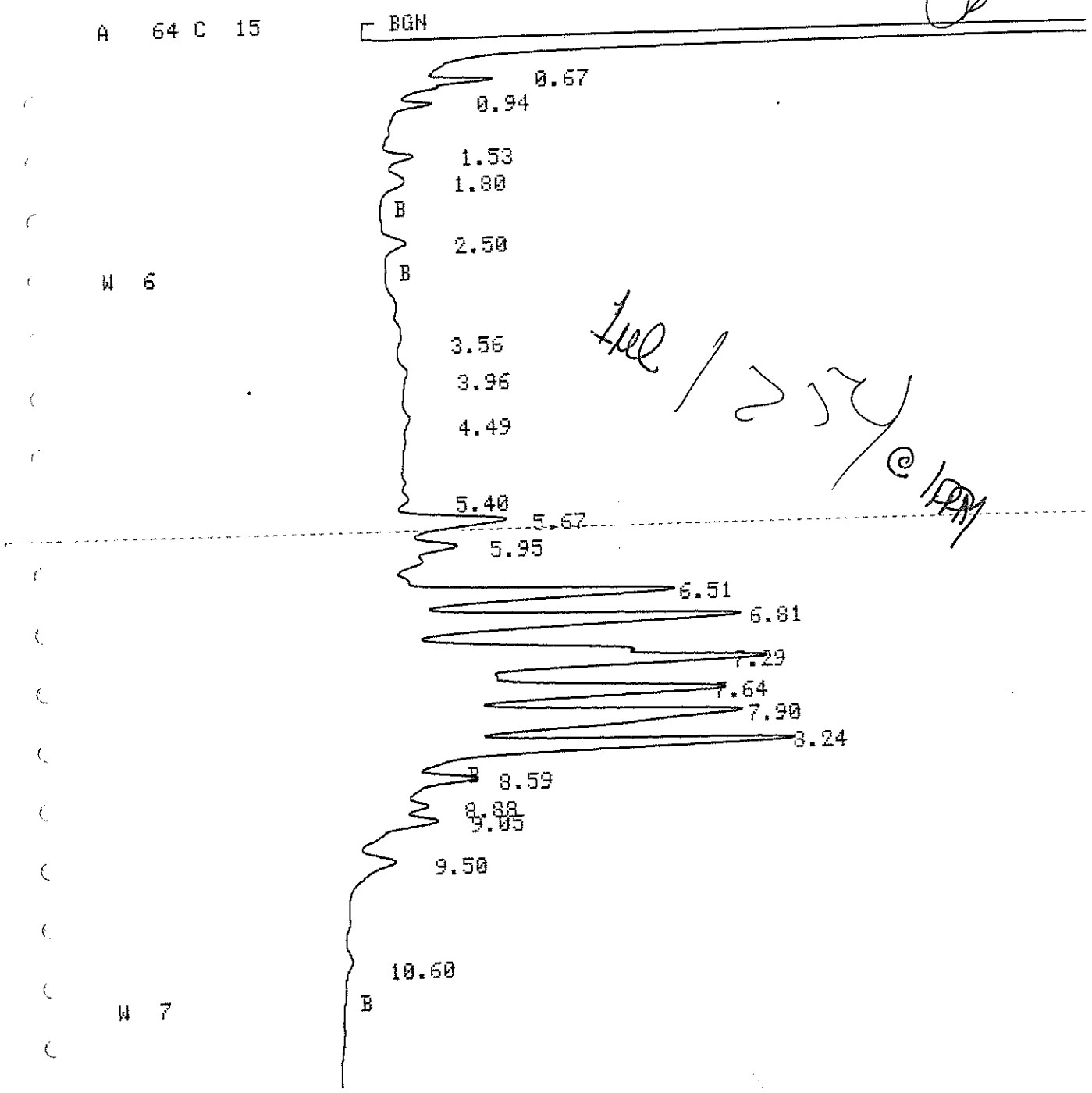
W 7

9 PEAKS > AREA/HT REJECT

RUN 15 7:31 91/03/12

METHOD 5 PCB

A 64 C 15



W 6

W 7

RUN 15 7:31 91/03/12

METHOD 5 PCB CALCULATION: %

RT	AREA	BC	AREA %
0.24	183.0837	T	37.5913
0.67	11.5487	T	2.3712

RUN 19 8:54 91/03/12

METHOD 5 PCB

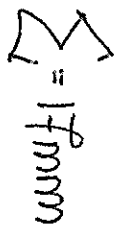
A 64 C .15

BGN

0.55
0.68
1.28
1.55
1.76
2.53
3.19
3.49
4.00
B
4.75
5.46
5.86
6.35
6.53
7.29
7.84
8.10
8.26
B
9.23
B

W 6

W 7



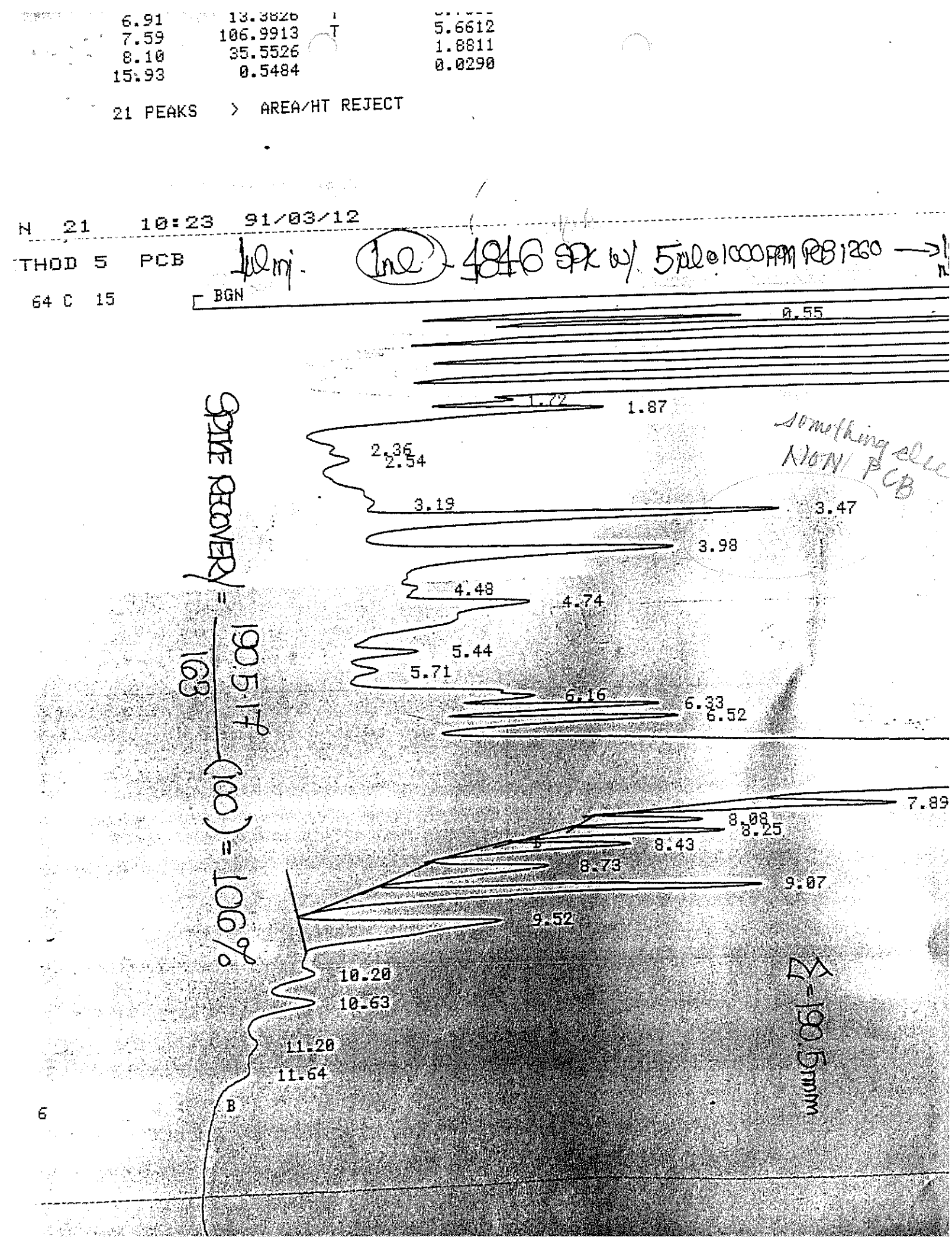
6.91	13.3826	T	5.6612
7.59	106.9913	T	1.8811
8.10	35.5526		0.0290
15.93	0.5484		

21 PEAKS > AREA/HT REJECT

N 21 10:23 91/03/12

THOD 5 PCB 1ul inj. Inc 4846 SPK w/ 5ml @ 1000 PPM PCB 1260 →

64 C 15



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